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LIQUID METAL AND HYDROGEN EMBRITTLEMENT OF NICKEL AND IRON-BASE AMORPHOUS ALLOYS.

Submitted by

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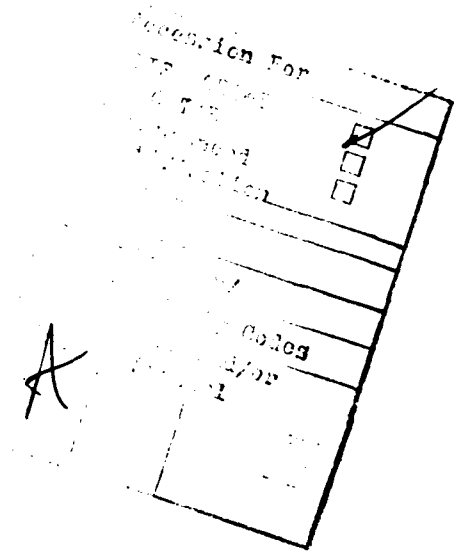

Abstract

Tensile and bend properties of nickel and iron-base amorphous alloys have been studied at 200°C in the presence of liquid lithium and in air. Nickel base alloys show severe embrittlement, except for Metglas 2826MB. The results are discussed on the basis of proposed mechanisms of LME and it is concluded that the embrittlement of amorphous alloys takes place by an enhanced shear mechanism. Hydrogen embrittlement also seems to occur by a similar process.

Introduction

Amorphous metallic alloys are known to demonstrate excellent resistance to general corrosion [1], due in part to the absence of grain boundaries or other microstructural imperfections connected with crystallinity. However, hydrogen embrittlement (HE) resulting from cathodic charging of iron-base amorphous alloys has been widely reported [2-4]. Recently, it has been shown for the first time that several iron-base amorphous alloys also suffer appreciable embrittlement when tested in liquid metal environments, e.g. Hg, Hg-In, or $Sn_{60}Pb_{40}$ [5]. The most significant feature of that work was the apparent demonstration that enhanced shear was the mechanism of embrittlement. The purpose of the present work was to conduct additional experiments, primarily in liquid lithium, to determine whether enhanced shear could be considered a general mechanism of LME. Studies of fracture of hydrogen-charged alloys have further demonstrated many features in common between HE and LME of amorphous alloys, leading to the conclusion that enhanced shear also may be responsible for hydrogen embrittlement.

Materials Studied

Experiments on hydrogen effects have been confined to four iron-base alloys: $Fe_{81.5}B_{14.5}Si_4$, $Fe_{81.5}B_{13.5}Si_{2.5}C_{2.5}$, $Fe_{40}Ni_{40}P_{14}B_6$ (Metglas 2826) and $Fe_{40}Ni_{38}B_{18}Mo_4$ (Metglas 2826MB). These alloys also have been subjected to testing in lithium, together with $Ni_{81}P_{19}$ (BNi-6) and $Ni_{18}Si_8B_{14}$ (BNi-3). FeBSi and FeBCSi alloys were supplied by the General Electric Co. The other alloys were obtained from Allied Chemical Corp.

Experimental Procedure

Tensile and bend tests were conducted on strip specimens, approximately 50μm thick for Ni base and 20μm thick for Fe-base; tensile specimens had reduced (2.5 mm) gage sections. These were shaped with a tensilgrind machine; edges were polished with No. 600 emery paper. Aluminum shims were used in the grips to enhance friction on the specimens. Tests at 200°C were carried out in air or under liquid Li, which was applied to the specimens with a soldering iron. All tests in Li were carried out at 200°C with the sample surrounded by a silicone oil bath. Bend tests were conducted on strips without reduced gage sections, following the procedure of Luborsky and Walter [6]. Ductility is calculated by measuring the radius of curvature of a coiled sample bent between parallel plates. The strain at fracture, λ_f, is given by

$$\lambda_f = \frac{t}{2r_f - t}$$

where r_f is the separation of the plates at fracture and t is specimen thickness.

Specimens also were cathodically charged in 1ℓ of 5 wt% H_2SO_4 in water, + 5 mg sodium arsenite. Charging was conducted at 1 mA/cm^2 for 15 minutes followed immediately by tensile testing.

All fractured samples were examined in a scanning electron microscope. Lithium was removed from the surface by washing with cold water; the specimen apparently is unaffected by the chemical reaction between Li and water. The specimens were then rinsed in acetone and dried.

Experimental Results

A. Tensile and Bend Tests in Lithium

Lithium had a drastic effect on the mechanical properties of several alloys, as demonstrated in the tensile data of Table I.

Table I

Fracture Stress at 200°C

Alloy	σ_F (N/mm^2)	
	No Li	Li
Metglas 2826	1067	100
BNi-3	1637	174
BNi-6	803	149

The tensile strengths of 2826, BNi-3 and BNi-6 were reduced by 90, 89 and 81%, respectively, at 200°C in the presence of lithium. Bend tests showed similar results; where strips of all alloys could be bent without limit in air, tests in lithium on the three alloys listed above resulted in $\lambda_f = 7.1 \times 10^{-4}$ to 1×10^{-2}. The three other test alloys, 2826MB, FeBSi and FeBCSi were unaffected by lithium.

B. Metallography and Fractography after Li Exposure

A notable and characteristic feature of the plastic deformation of amorphous alloys is the appearance of shear bands on the surface just prior to fracture. These bands are sometimes quite wavy, e.g. at the crack tip in FeBCSi deformed in bending in air, Figure 1. In the presence of liquid metal fracture occurred along the same shear bands, see Fig. 2a) and b). The fracture surfaces of alloys broken in the presence of Li were very brittle in appearance at low magnification, Fig. 3a). However, at higher magnification, Fig. 3b) there is considerable evidence of local plastic deformation, particularly near the sample edges. A particularly striking association between metal-induced cracks and a shear band may be noted in Fig. 3c). Previous work on FeBCSi tested in mercury revealed an even more striking result, Fig. 4 [5]. The brittle-appearing fractographic features seen at low magnification, Fig. 4a), were transformed into fine "veining" patterns, characteristic of samples fractured in air, Fig. 4b), although the cell-like features were finer in the presence of the liquid metal. Fractured BNi-3 also reveals veining patterns both in air Fig. 5a) and in Li, Fig. 5b), again with the size of cells reduced in the liquid metal. Similar results also have been noted after hydrogen charging of FeBSi, see Fig. 6. Note the rather flat facets in Fig. 6a), which give way to very small cells in Fig. 6b).

In all of the cases cited in Table II and Fig. 2, embrittlement was accomplished by supplying liquid Li to the tensile face of the bend specimen. Experiments conducted with Li on the compression side have, however, produced equivalent results. This totally unexpected result has not been previously achieved with crystalline metals.

TABLE II

Bend Ductility at 200°C

Alloy	Strain to Fracture in Li
2826	$\sim 7.1 \times 10^{-4}$
BNi-3	$\sim 1.7 \times 10^{-3}$
BNi-6	$\sim 1.0 \times 10^{-2}$
2826MB*	Not Embrittled
FeBSi*	Not Embrittled
FeBCSi*	Not Embrittled

* Alloys did not fracture in bending in air.

Discussion

Although many mechanisms have been proposed by which atoms of a liquid metal may facilitate fracture in crystalline metals, two have been considered the most likely: a decohesion model [7,8] and an enhanced shear model [9,10]. These two alternatives are depicted schematically in Figs. 6a) and b), respectively. The decohesion [11,12] and enhanced shear [13,14] models also have been applied to hydrogen embrittlement, leading in the last few years to a lively debate concerning the merits and demerits of each approach. The decohesion model, as applied to LME, can be criticized largely upon the grounds that a) it does not predict "specificity" of embrittlement; b) the precise nature of the interaction leading to decohesion remains unknown; c) since the decohesion mechanism does not incorporate time dependence, it cannot account for delayed failure in the presence of liquid metals [15]; and finally d) fracture surfaces that display characteristics of cleavage at low magnification reveal very fine dimples at high magnification [9,10].

The latter observation is one of the most striking anomalies of LME, and has been taken as strong evidence for high local plasticity arising from enhanced shear at the crack tip arising from the metal embrittler atoms. This model also has its deficiencies, since there is no apparent means by which the environment can reach microvoids ahead of the crack tip as they grow and coalesce to form the observed dimples. The enhanced shear mechanism also offers no insight into "specificity", nor does it explain delayed failure.

In spite of the shortcomings of the two principal proposed mechanism of LME, alternative explanations based upon rapid stress-assisted dissolution [16,17] or formation of brittle layers at the crack tip by interdiffusion of embrittled and substrate atoms [18] have not been any more convincing. The wide occurrence of transcrystalline failure in polycrystals and single crystals exposed to metal environments clearly renders mechanisms associated with short circuit diffusion paths as highly unlikely, except in very special cases.

A major advantage of working with amorphous metals is the lack of complicating structural inhomogeneities, most particularly grain boundaries. In fact, the only evidence of heterogeneity in plastic deformation is the occurrence of very high strains in shear bands, even in inert environments. Since there is no possibility of invoking a decohesion mechanism in inert environments, it clearly is unlikely to be applicable to metal or hydrogen-induced fractures. This expectation is fully supported by the clear evidence for fracture along shear bands in the presence of embrittling environments, e.g., Fig. 2.

Undoubtedly the most significant finding of this study is the achievement of LME with liquid applied to the compression side of the sample. This finding is, of course, totally incompatible with a decohesion mechanism. Whereas the experimental observations are clearly consistent with the enhanced shear model, the possibility of a very rapid chemical reaction between Li and the embrittled substrates must be considered.

For example, Li is known to react with carbides at grain boundaries in crystalline steels, leading to a severe deterioration in fracture strength and ductility [20]. In the present investigation, carbon content cannot be a factor, since the only carbon-containing alloy, FeBCSi, was not embrittled by Li. The fact that alloy 2826 was severely embrittled by Li, whereas the very similar alloy 2826MB was not (MB contains 4% Mo) seems to rule out the possibility that a very high diffusion rate enables Li to penetrate through some alloys, but not others.

Moreover, there was not evidence of significant chemical reaction on the surfaces of any of the embrittled foils, and the fractographic features were distinct, as shown in Figs. 3a) and b). We have succeeded also in embrittling FeBCSi with Hg-In on the compression side of a bend sample. The rapid formation and fracture of an embrittled layer due to Li penetration also must be considered. However, once again there does not seem to be any reason why such a layer would form in alloy 2826 but not in alloy 2826MB. Therefore, corrosion and/or diffusion-related phenomena do not seem applicable to LME of these alloys.

On the basis of the above analysis, together with the observation that fracture surfaces of embrittled samples display evidence of localized inelastic flow, and that cracks invariably form and propagate along shear bands, we conclude that enhanced shear can account for all reported cases of LME in amorphous metals. Whereas the evidence is less definite in the case of cathodically charged foils, the presence of a fine veining pattern on the fracture surfaces of hydrogenated foils suggests that the same mechanism might be operative.

Acknowledgements

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References

1. K. Hashimoto, M. Naka, T. Musumoto and S. Shimodaira, Corr. Sci., 16, (1976) 61.

2. A. Kawashima, K. Hashimoto and T. Masumoto, Scripta Met., 14 (1980), 41.

3. R.K. Viswanadham, J.A.S. Green and W.G. Montague, Scripta Met., 10, (1976), 229.

4. A. Kawashima, K. Hashimoto and T. Masumoto, Corrosion, 36,(1980), 577.

5. S. Ashok, N.S. Stoloff, M.E. Glicksman and T. Slavin, Scripta Met., 15 (1981), 331.

6. F.E. Luborsky and J.L. Walter, J. Appl. Phys., 47,(1976), 3648.

7. N.S. Stoloff and T.L. Johnston, Acta Met., 11, (1963), 251.

8. A.R.C. Westwood and M.H. Kamdar, Phil. Mag., 8, (1963), 787.

9. S.P. Lynch, Scripta Met., 13, (1979), 1051.

10. S.P. Lynch, Acta Met., 29 (1981), 325.

11. A.R. Troiano, Trans. ASM, 52 (1960), 54.

12. R.A. Oriani and P.H. Josephic, Acta Met., 22, (1974), 1065.

13. C.D. Beachem, Stress Corrosion Cracking and Hydrogen Embrittlement of Iron Based Alloys, NACE, Houston, 1975, 376-381.

14. S.P. Lynch and N.E. Ryan, Proc. Sec. Int. Conf. on Hydrogen in Metals, Paris (1977), Paper 3D12.

15. P. Gordon, submitted to Met. Trans. A, (1981).

16. W.M. Robertson, Met. Trans., 1,(1970), 2607.

17. E.E. Glikman and Yu V. Goryunov, Fiz. Khim. Mekh. Meter., 14,(1978), 20 (Sov. Mat. Sci.).

18. M.A. Krishtal, Sov. Phys. Dokl., 15,(1970), 614.

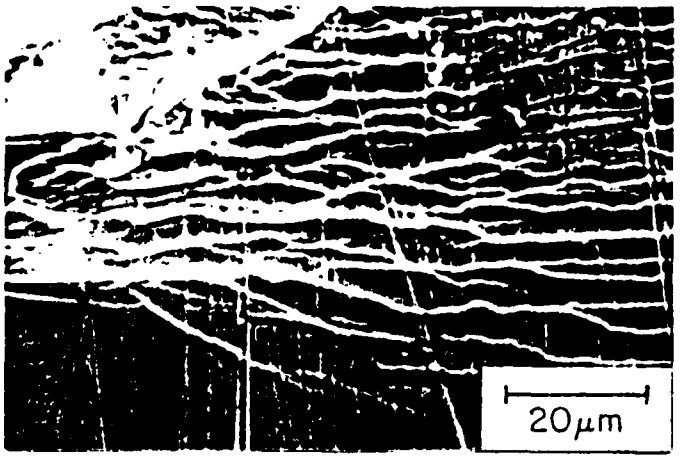
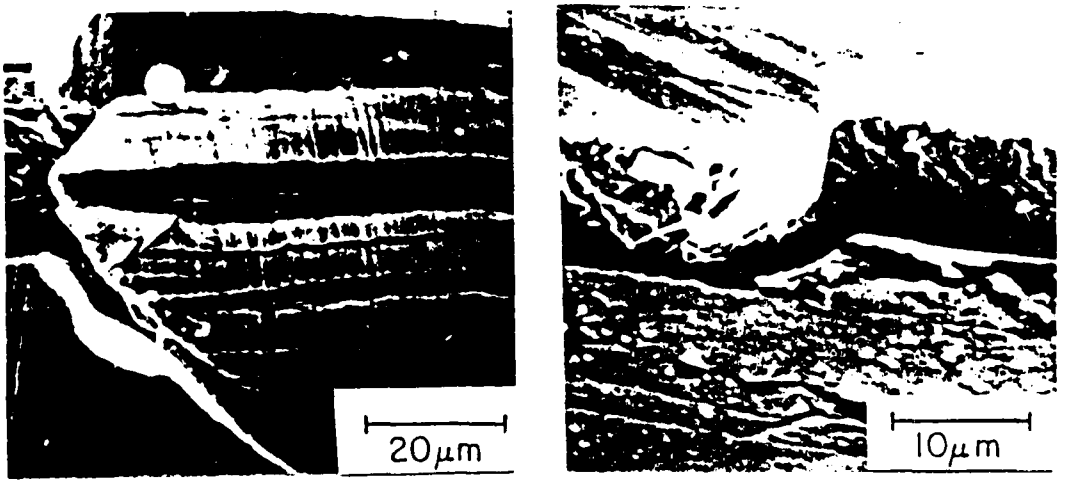


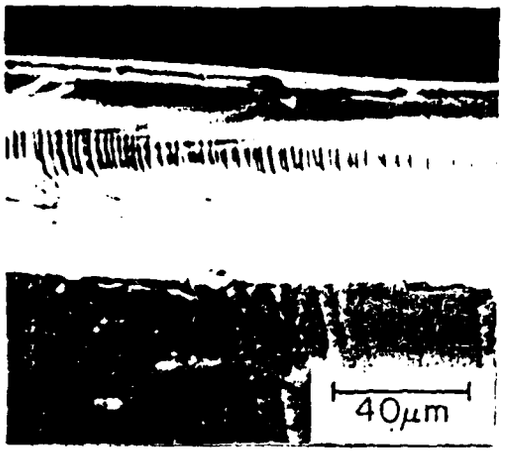
Fig. 1. Shear bands near crack tip in bend specimen of amorphous FeBCSi tested at 25°C.



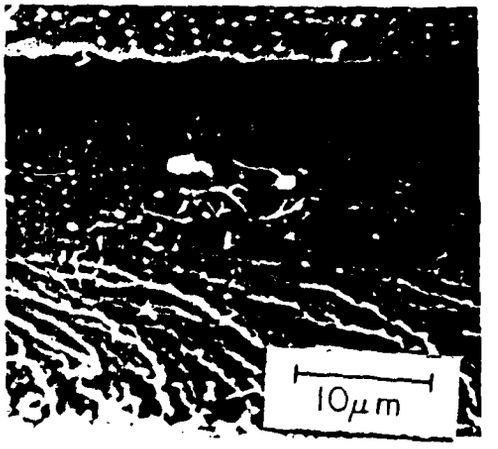
a) $FeBCS_i$ in Hg-In

b) Metglas 2826 in Li

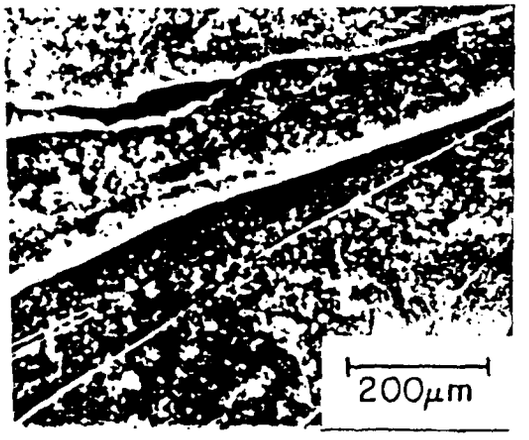
Fig. 2. Shear bands near crack tip in bend specimen of amorphous alloys tested in the presence of liquid metals.
a) FeBCSi in Hg-In.



a) Brittle appearance at low magnification



b) Local plastic deformation observed at high magnification



c) Shear bands and cracks due to Li

Fig. 3. Fractograph of Metglas 2826 tested in bend at 200°C in the presence of Li.

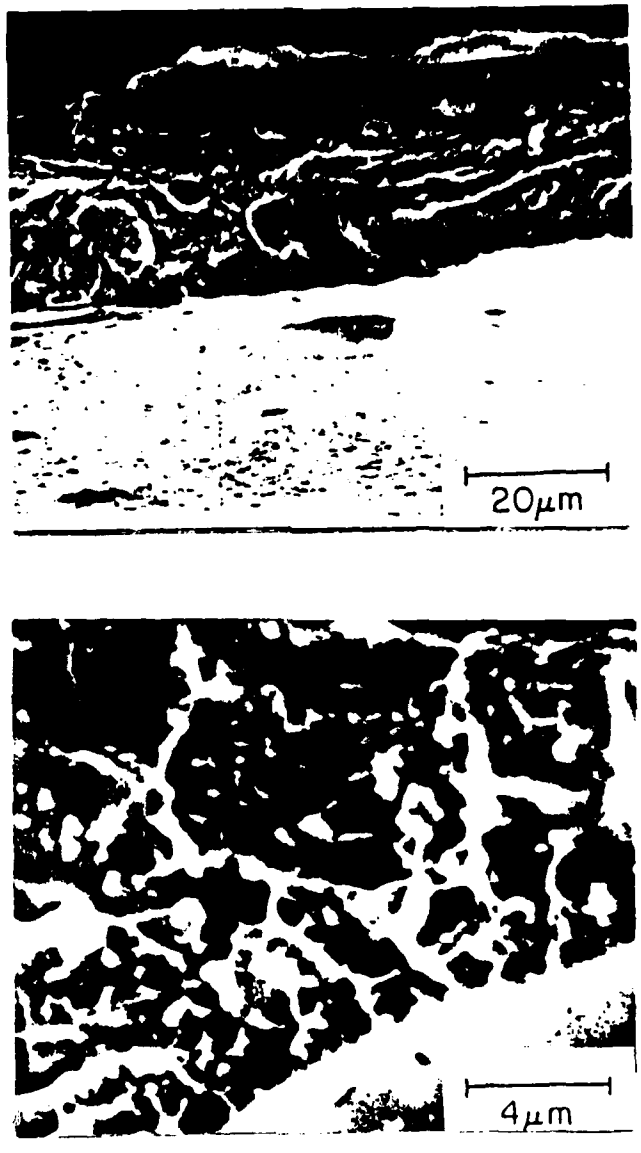


Fig. 4. Fractographs of amorphous FeBCSi tested in tension at 25°C in the presence of Hg-In. a) Flat facets at low magnification; b) fine veining patterns on facets observed at high magnification.

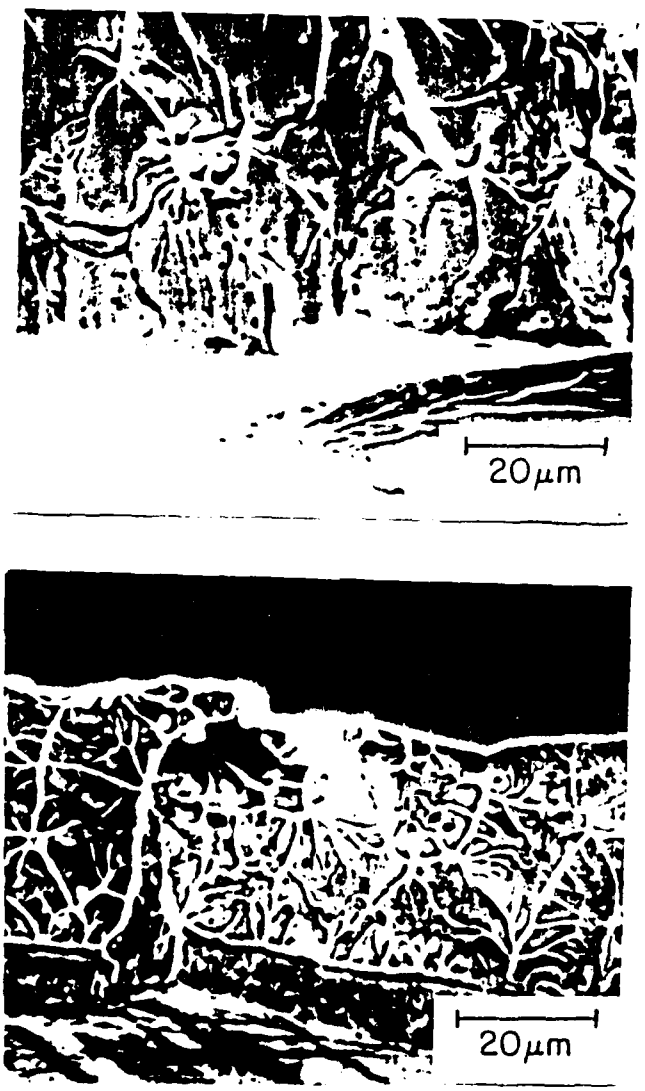


Fig. 5. Fractographs of BNi-3 tested in tension at 200°C.
a) air; b) lithium.

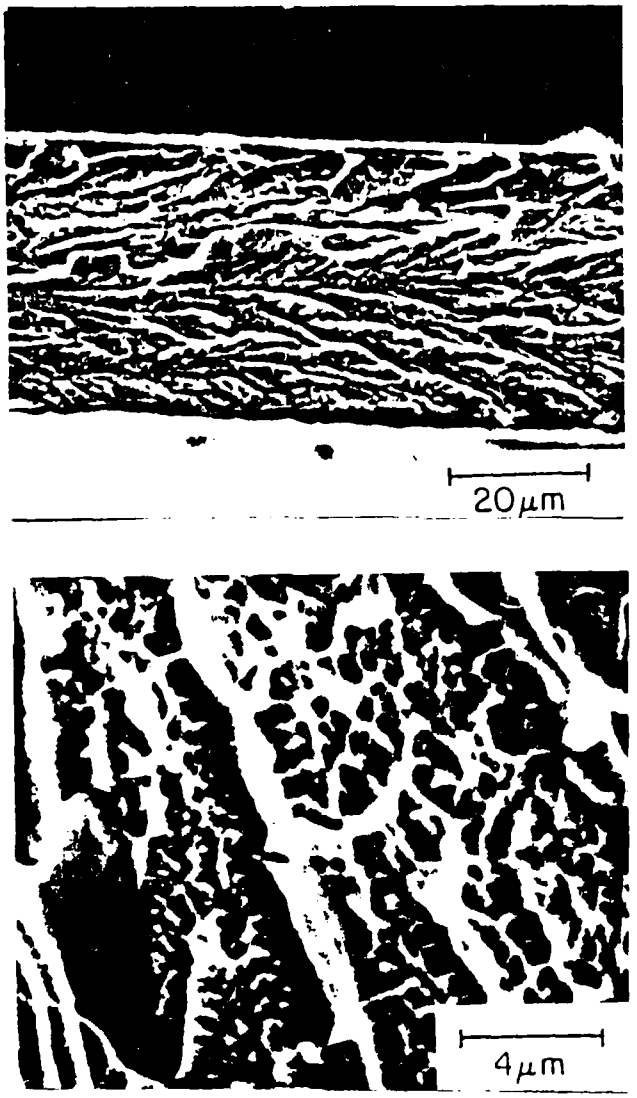


Fig. 6. Fractographs of amorphous FeBSi tested in tension after charging with hydrogen. a) Flat facets at low magnification; b) small cells on facets observed at high magnification.

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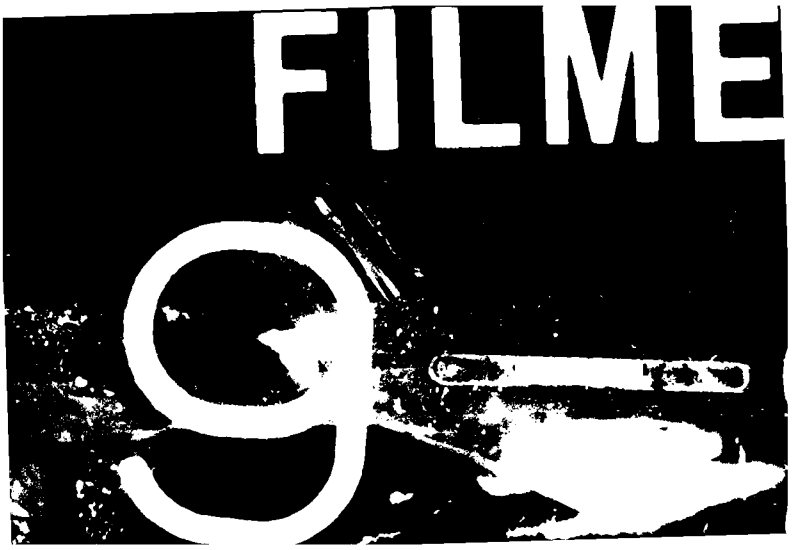
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